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Perovskite-like catalysts $LaBO_3$ (B = Cu, Fe, Mn, Co, Ni) for wet peroxide oxidation of phenol

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ABSTRACT

The catalytic behavior of perovskite-like oxides $LaBO_3$ (B = Cu, Fe, Co, Ni, Mn) prepared by the Pecini method were examined in wet peroxide oxidation of phenol as a model organic substrate. The study showed the activity of only $LaCuO_3$ and $LaFeO_3$ perovskite-like catalysts, Cu-containing catalysts being more active, though Fe-containing being more stable. The leaching test proved the heterogeneous nature of the catalyst action. The long-term experiments revealed the acceptable stability of the $LaFeO_3$ catalyst. XRD studies of the spent samples demonstrated the stability of the perovskite-like structure of the catalysts during the reaction. The assumption about the nature of the active sites and the possible mechanism of the reaction was proposed based on of the XPS study.

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1. Introduction

While the expansion of fresh water consumption worldwide results in a continuous decrease in the quality and quantity of the available resources, the development of new effective methods for cleaning of industrial wastewater from various pollutants is of vital importance [1,2]. In the recent years, a number of technologies (biological, thermal, chemical) have been developed for removal of toxic organic compounds from industrial wastewater [1,3–5]. The process of catalytic wet peroxide oxidation (CWPO) is considered an alternative for the treatment of wastewater with moderate and relatively low concentrations of high-toxic organic compounds. Hydrogen peroxide does not produce harmful by-products and, therefore, is a non-toxic and ecologically friendly oxidant [6,7].

Phenol and phenol derivatives are among most abundant organic contaminants, which are toxic at rather low concentrations and stable to the biodegradation [1,8]. For this reason phenol is a usual model substrate in developing methods for wastewater treatment.

Fenton-like systems with aqua-ions of transition metals mainly iron ions ($Fe^{2+}/Fe^{3+}/H_2O_2$) as catalysts are widely used for generation of hydroxyl radicals which are highly active oxidants of many organic compounds including phenol and phenol derivatives [9]. Even though transition metal salts are highly active to oxidative destruction of organic pollutants with hydrogen peroxide, the homogeneous oxidation processes have some drawbacks such as a narrow pH range of the catalytic action, the catalyst deactivation in the presence of complexing substances, necessity of the catalyst regeneration and of the removal of iron compounds from the cleaned water. The use of solid catalysts should solve mentioned problems. Hence, it is practically important to develop a solid catalyst with the high activity and stability to deactivation and to metal leaching.

Various transition metal containing oxide materials were tested as solid catalysts for CWPO; these were zeolites, mixed oxides and hydroxides, pillared clays etc. [10–13]. However, even though some of the catalysts were highly active, their stability often was unsatisfactory due to leaching of the active component in the aggressive aqueous oxidative medium.

Perovskite-like oxides $LaMeO_3$ are among the most active catalysts for CWPO, they are highly active and stable in aggressive media [14]. Therefore, the current activities are aimed at studying potential applications of perovskite-like oxides for the catalytic oxidation [15]. The catalytic versatility of these oxides is based on their high stability at high temperature and in an aggressive medium, as well as on the stabilization of transition metal ions in unusual oxidation states and on the high oxygen mobility in the perovskite structure.

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Fe-, Cu-, Mn-, Co- and Ni-containing perovskite-like oxides prepared by various methods were catalytically active in aqueous media to the reactions such as decomposition of hydrogen peroxide [16–18]; catalytic destruction of ketopropionic acid with ozone [19]; wet air catalytic oxidation of organic substrates (salicylic acid [20], lignin [21–23], stearic acid [24] and phenol [25–27]); as well as photocatalytic oxidation of acetic acid using Fe-, Mn-, Co-, Ni-, Cu-containing perovskites supported on cordierite monoliths [28]. There are only two publications devoted to the studies of catalytic properties of perovskite-like oxides in the CWPO. Perovskites $LaTi_{1-x}Cu_xO_3$ and $LaFeO_3$ were highly active to oxidation of phenol with hydrogen peroxide [29,30]. However, a very low stability to the copper leaching was characteristic of $LaTi_{1-x}Cu_xO_3$ (more than 20% of the initial Cu content was leached to the solution), while $LaFeO_3$ was much more stable (less than 0.27% of the initial Fe content was leached to the solution).

The present work was aimed at the systematic studies of perovskite-like oxides $LaBO_3$ (B = Fe, Cu, Mn, Ni, Co) as catalysts for CWPO of phenol. The catalysts were prepared by the Pecini method; an advantage of the method is that the metal cations remain bounded in the produced polymer matrix. As a result, the processes of segregation, crystallization and thermal destruction of initial reactants to form metal oxides are prevented in the course of the solution evaporation. This method allows stoichiometric oxides to be prepared under milder conditions as compared with the ceramic method and without wastewater effluents against the precipitation method. In addition, the method leads to the formation of films strongly anchored on the support surface that is practically important.

Particular attention was paid to exhaustive studies of the activity of the catalysts after multiple reusing catalytic test as well as to the phase stability and electron state of catalytically active metals in the perovskite structure. XRD and XPS techniques were used for characterization of the samples before and after the reaction. XPS data confirmed redox transitions occurring in $LaFeO_3$ and $LaCuO_3$ catalysts during the catalytic reactions and an increase in the surface concentration of oxygen which enhance the degradation rate of the phenol molecule after successive catalytic cycles.

2. Experimental

2.1. Catalyst preparation

The Picini method was used for preparing all samples under study ($LaFeO_3$, $LaCuO_3$, $LaNiO_3$, $LaCoO_3$, $LaMnO_3$). Magnesium, cobalt, nickel, iron, copper and lanthanum nitrates were used as initial reactants for synthesis of the samples. The nitrates containing cations in the stoichiometric quantity for synthesis of 15 g of the product were dissolved in water (50–100 mL); then citric acid (4 mL, 2 g mL^{-1}) and ethyleneglycol (3 mL) added. The resulting solution was evaporated in a sand bath. At the end of the evaporation, the mixture got inflamed to produce an x-ray amorphous precursor of perovskite; the precursor was calcined in air at 900 °C for 4 h.

2.2. Characterization of the catalysts

Phase compositions of samples were determined by x-ray diffraction (XRD) using a Bruker D8 diffractometer (Germany) with Cu$K\alpha$ (λ = 1.5418 Å) radiation in 0.05° intervals in the 2θ range between 20 and 80°. The phase composition stability at high temperature (up to 900 °C) was studied in air by high-temperature XRD using an X-ray chamber HTK-16 (Anton Paar, Austria).

N_2 adsorption isotherms at –196 °C were used for textural studied with an ASAP-2400 (Micromeritics, USA) instrument. All the samples to be studied were pre-degassed in vacuum at 150 °C. Specific surface areas were determined using the classical BET model.

XPS technique was used for studying surface composition and electron states of copper, iron and lanthanum in $LaFeO_3$ and $LaCuO_3$; the spectra were acquired using a SPECS photoelectron spectrometer with MgK_a radiation (hn = 1253.6 eV, 200 W). The binding energies scale was preliminarily calibrated using the core levels of the $Au4f_{7/2}$(84.0 eV) and $Cu2p_{3/2}$(932.67 eV) peaks. The binding energy of peaks was calibrated by the position of the C1s peak (BE = 284.8 eV) corresponding to the surface hydrocarbon-like deposits (C—C and C—H bonds) [31]. For the survey spectra the pass energy of the analyzer was 50 eV, while for the narrow spectral regions −20 eV. The ratio of surface atomic concentrations of the elements was calculated from the integral intensities of photoelectron peaks corrected by corresponding atomic sensitivity factors [32].

2.3. Catalytic testing

The phenol oxidative destruction was carried out in a thermostated three-necked glass slurry reactor at 30 and 50 °C under continuous stirring (900 rpm) with a magnetic stirrer. The concentrations of phenol and hydrogen peroxide were 0.01 and 0.7 mol L^{-1}, respectively. The quantity of hydrogen peroxide was taken as large as 5.5 times of the oxidative equivalents for oxidation of phenol to carbon dioxide and water. An approximately constant (±10% of the initial concentration) H_2O_2 concentration was maintained all along the reaction. Before starting the experiment, the reaction mixture was acidified by HNO_3 to a pH 3, pH being not corrected during the reaction. Then, a catalyst sample of 5 g L^{-1} or 0.1 mM solution of nitrate of iron (in the case of a homogeneous reaction in the presence of dissolved iron ions) was added. At regular time intervals, aliquots (1 mL) were taken from the reactor to monitor the substrate and H_2O_2 concentrations. Samples were stabilized by adding ethanol at the ratio 1:1.

A total of organic carbon (TOC) content was determined in filtered aliquots using a Shimadzu TOC Analyzer TOC-VCSH (Japan) upon complete destruction of phenol except the cases of a very low catalyst activity that made it unreasonable to expect completing of the reaction.

The catalyst stability to leaching the active component was estimated based on the ICP-AES (Optima 4300 DV, PerkinElmer Inc., USA) measurement of quantity of leached copper, iron, manganese, cobalt, nickel and lanthanum in the reaction solution.

The contribution of dissolved copper ions (homogeneous component) to the catalytic activity was identified as follows. After the reaction over a solid catalyst was finished, the catalyst suspension was filtered out using acetatecellulose membrane filters (pore diameter 0.20 μm). The filtrate was placed in a thermostated reactor, the substrate and hydrogen peroxide were added in the necessary quantities. The reaction was conducted under conditions identical to the heterogeneous catalytic reaction.

Multicycle tests of catalysts $LaCuO_3$ and $LaFeO_3$ were conducted as follows: As the oxidation cycle was over, the reaction solution was extracted with a syringe, and the necessary quantities of the solution of the substrate to be oxidized and hydrogen peroxide were added to the wet catalyst. The reaction was conducted under identical conditions. There only were three successive cycles of phenol oxidation over the $LaCuO_3$ catalyst. As to $LaFeO_3$, the catalyst was centrifuged after 10th, 20th, 30th, 40th cycles of phenol oxidation, washed with distilled water, dried at 100 °C in a drying box, calcined in air at 180 °C and weighed. The catalyst was used for the next oxidation cycle under identical conditions.

The influence of pH on the oxidation kinetics was studied with the $LaFeO_3$ and $LaCuO_3$ catalyst over the pH range between 3 and 8. A NaOH solution was added to the phenol solution to obtain

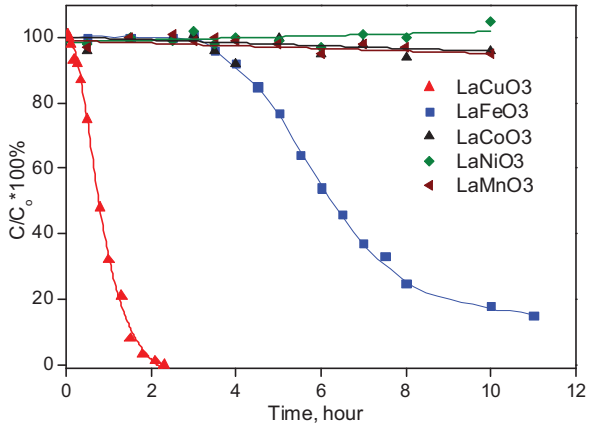

Fig. 1. Kinetic curves of phenol CWPO over catalysts (pH 3, 30 °C).

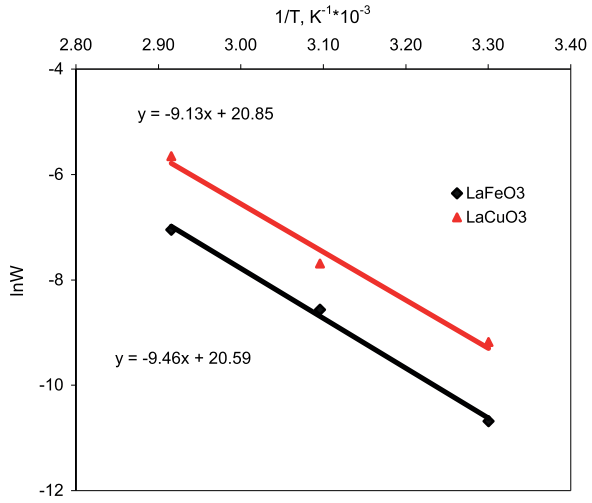

Fig. 2. The Arrhenius plot of the reaction rate vs temperature over $LaCuO_3$ and $LaFeO_3$ catalysts (pH 3, 30–70 °C).

required pH and was not corrected during the reaction. The reaction started upon addition of a catalyst sample.

2.4. Analytic methods

All chemicals and reagents utilized in this study were of analytical grade. Milli-Q water (Millipore, France) was used for preparing all the solutions.

A spectrophotometric method based on the absorption of a titanium complex (λ = 410 nm) was used for determining the concentration of H_2O_2 [33]. For this operation was used UV/ Vis spectrophometer Uvikon 923 (Kontron Instruments, USA).

The concentrations of phenol were measured by HPLC using a Shimadzu LC-20A chromatograph with a diode array detector and Phemomenex Synergi 4u Hydro-RP 80A column (250 × 4.6 mm, 4 μm). Analytic conditions for determination of phenol concentration: eluent 65 vol.% H_2O + 35 vol.% acetonitrile, flow rate 0.7 mL min^{-1}, column temperature 30 °C.

3. Results and discussion

3.1. Catalytic properties and stability of perovskites during the peroxide oxidation of phenol

A considerable decrease in the phenol concentration was only observed over $LaFeO_3$ and $LaCuO_3$, the catalyst $LaCuO_3$ being more active (Fig. 1). $LaNiO_3$, $LaMnO_3$, $LaCoO_3$ were inactive to the peroxide oxidation of phenol, while the decomposition rates of hydrogen peroxide over these catalysts were 5–10 and 50–100 times as high as those over $LaCuO_3$ and $LaFeO_3$, respectively. Over Ni-, Mn- and Co-containing catalysts pH of the reaction solutions were observed to increase up to 6 and above due to, apparently, the low stability of these catalysts to La leaching (Table 1). The rise of pH in the solution usually causes an increase in the rate of hydrogen peroxide destruction and shortening of the lifetime of hydroxyl radicals those results in the low efficiency of oxidation of organic substrates [34,35]. In experiments with $LaNiO_3$ we tried to maintain pH equal to 3 by adding a nitric acid solution. However, pH of the solution was between 6.1 and 6.4 even after multiple addition of the acid till its concentration equal to 0.1 M. While $LaCoO_3$, $LaMnO_3$, $LaNiO_3$ did not show any catalytic activity to the target reaction, these sample were not further studied.

There are two regions in the kinetic curves of decreasing phenol concentration over $LaCuO_3$ and $LaFeO_3$: a slow region (induction period) and a fast region where the phenol concentration decrease according to the zero order kinetics (Fig. 1). Similar kinetic curves also were typical for oxidation of formic acid over Cu- and Fe-ZSM-5 zeolites [36]. Over $LaCuO_3$, the induction period is ca. 10 min long at 30 °C, and the specific activity along the straight region is 1.2 mmol h^{-1} g_{cat}^{-1} (Fig. 1), the quantity of copper leached was 0.345 mM (21.9 mg L^{-1}) or 1.73% of the total copper content in the catalyst. Over $LaFeO_3$, the induction period of ca. four hours is identified, and the specific activity in the straight region is 0.28 mmol h^{-1} g_{cat}^{-1} at 30 °C, the quantity of iron leached was 0.093 mM (5.2 mg L^{-1}) or 0.45 % of the total iron content in the catalyst. The quantities of lanthanum leached were not so different (0.23% (0.045 mM) for $LaCuO_3$ and 0.63% (1.29 mM) for $LaFeO_3$ (Table 1)). The total organic carbon was 14% of the initial phenol quantity after the reaction over $LaCuO_3$ and 67% over $LaFeO_3$.

3.2. The influence of test conditions

The influence of temperature on the rate of phenol oxidation over $LaFeO_3$ and $LaCuO_3$ was studied at 30, 50 and 70 °C. Emphasize that the induction periods in the kinetic curves shortened considerably as the temperature elevated: the induction period took 3 h at 30 °C; less than 15 min at 50 °C but was not observed at 70°. The effective activation energies (E_a) calculated using the Arrhenius plot (Fig. 2) for $LaCuO_3$ and $LaFeO_3$ are close to one another (75.9 and 78.6 kJ mol^{-1}, respectively). We failed to find any literature data on the activation energy of phenol peroxide oxidation over the perovskite-like catalysts. Most well studied catalysts for this reaction are ZSM-5 zeolites. The activation energy for the zeolites catalysts is in the range of 50–96 kJmol^{-1}. [37,38]. Thus, the activation energy observed in this work correlate with the literature data related to the most active zeolite catalysts (Fig. 3).

Inspection of the metal contents in the reaction solution after completing the reaction showed that the catalyst stability to leaching copper, iron and lanthanum ions did not change upon temperature elevation. For example, the quantities of Fe^{3+} ions leached from the $LaFeO_3$ to the solution at 30 and 50 °C were 0.45 and 0.44%, respectively, of the initial iron contents in the perovskite. Over $LaCuO_3$, the quantities of copper ions were 1.22–1.73% of the initial contents in perovskite at 30, 50 and 70 °C, respectively, the maximal quantity (1.73%) being observed at 30 °C. At the same time, only negligible increase in the quantity of lanthanum in the solution was observed upon rising the temperature. Thus, the stability of $LaFeO_3$ and $LaCuO_3$ to leaching the active metals to the solution in the temperature range 30–70 °C was found satisfactory.

An increase pH in the range 3–8 results in a lengthening of the induction period over both catalysts. The reaction rate along the

Table 1
Analysis of the reaction solutions after the catalytic wet peroxide oxidation (CWPO) of phenol over perovskite-like catalysts (pH 3, 30 °C).

Catalyst	Characteristics of the reaction solution after the experiment					
	pH	[Me] in filtrate, mM	[Me] in filtrate, %	[La] in filtrate,mM	[La] in filtrate, %	X_{TOC}, %
$LaCuO_3$	3.07	0.345	1.73	0.045	0.23	86
$LaFeO_3$	3.10	0.093	0.45	0.129	0.63	44
$LaMnO_3$	6.4	0.002	0.01	0.180	0.87	0
$LaNiO_3$	6.2	0.324	1.60	0.270	1.33	0
$LaCoO_3$	6.5	0.514	2.54	0.549	2.72	0

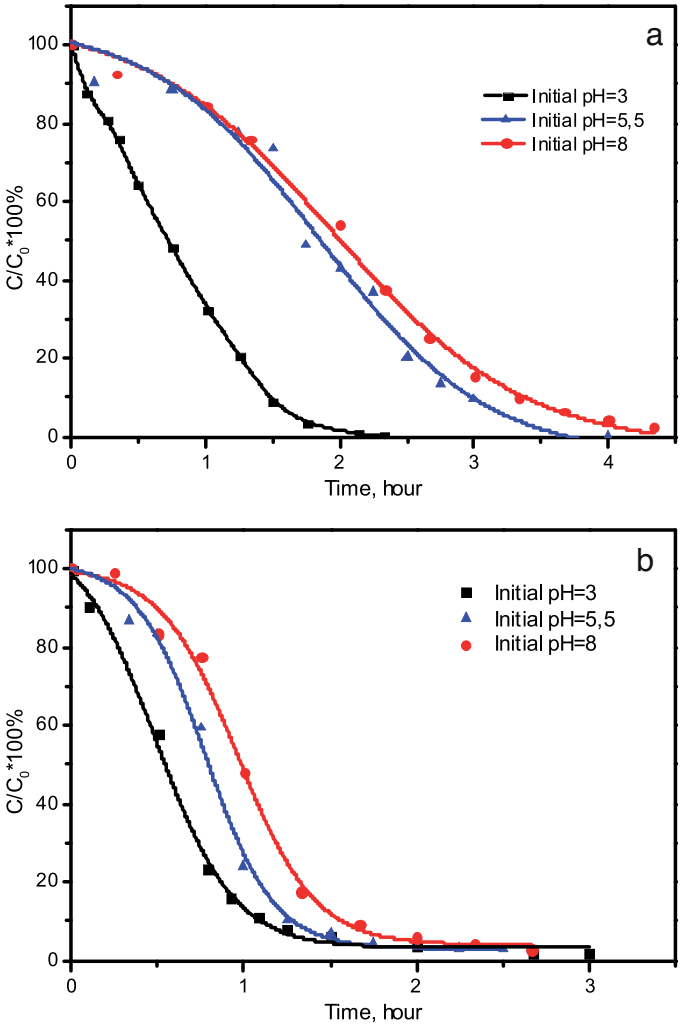

Fig. 3. Kinetic curves of phenol CWPO at different pH over of $LaCuO_3$ (a) (pH 3–8, 30 °C) and $LaFeO_3$ (b) (pH 3–8, 50 °C).

straight region in the kinetics is practically independent of pH. This phenomenon may be accounted for the formation of acidic intermediates (acetic, malonic, formic, etc. acids) due to the slow phenol oxidation during the induction period. The formed acids cause lowering pH to the optimal level between 3 and 4 to favor the fast oxidation of phenol.

It is well-known that the economic viability of the CWPO process is linked to the amount of used hydrogen peroxide and their efficient use. The high excess of hydrogen peroxide in this work was used in order to fix its concentration for the correct kinetic measurements. The typical H_2O_2 concentration in this work was 0.7 M. The reaction rate over $LaFeO_3$ under these conditions (50 °C) was 0.1304 mmol L^{-1} min^{-1}. We conducted additional experiments over $LaFeO_3$ at lower H_2O_2 concentrations (0.34 and 0.16 M). Note that the latter concentration is close to the stoichiometric concentration. Reaction rates calculated for these experiments appeared to be 0.0643 and 0.0324 mmol L^{-1} min^{-1}. These results showed four-fold decrease in the H_2O_2 concentrations resulted in a decrease in the reaction rate to one fourth. The reaction order equal to 0.94 was determined as the slope of lnW-lnC straight line (Fig. S1). These results are consistent with the data reported by Sotelo et. al. who studied $LaTi_{1-x}Cu_xO_3$ in the CWPO of phenol [29]. Beside similar reaction order (0.8–1) on H_2O_2 was found for zeolites catalysts in CWPO of phenol in our previous work [37]. These experiments showed the possibility of carrying out effective destruction of organic substrates at the stoichiometric amount of hydrogen peroxide. The amount of the oxidant in the reaction medium, at least within the range under study, does not effect the redox transitions on the catalyst surface which are responsible for the enhancement of the activity.

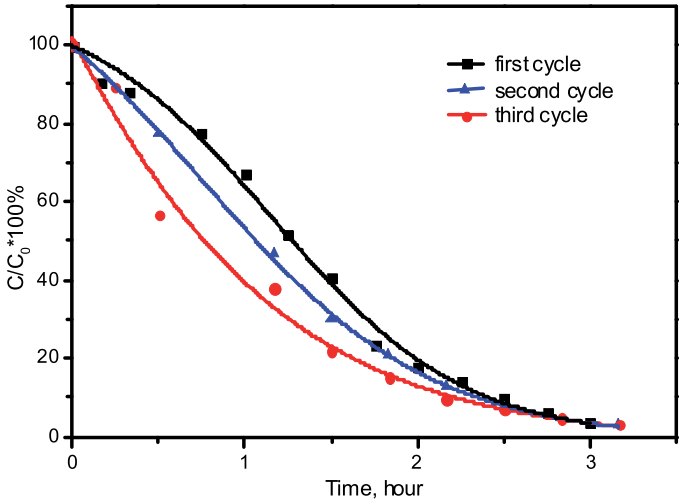

Fig. 4. Kinetic curves of phenol peroxide oxidation over $LaCuO_3$ during long-term tests (pH 3, 30 °C).

3.3. *Multicycle testing of $LaCuO_3$ and $LaFeO_3$*

Three cycles of testing $LaCuO_3$ at 30 °C showed that the rates of oxidation along the straight regions of the second and third cycles do not decrease but somewhat increase (Fig. 4). The reason of this phenomenon will be discussed below.

In considering the facts of more severe ecological standards with respect to copper content in water, a higher price for copper and four times lower stability of copper during the reaction, we decided to use the $LaFeO_3$ for long-term multicycle experiments. The five-cycle phenol oxidation at 30 °C over $LaFeO_3$ showed that the induction period starts shortening (to ca. 1 h) as early as the second cycle and takes ca. half an hour in the third and the subsequent cycles (Fig. 5a). Along the straight regions of the kinetics, the specific catalytic activity increased in the second cycle and remained almost unchanged in the subsequent cycles (0.40–0.42 mmol h^{-1} $g_{cat}{}^{-1}$), i.e. in the second through fifth cycles the Fe-containing catalyst was

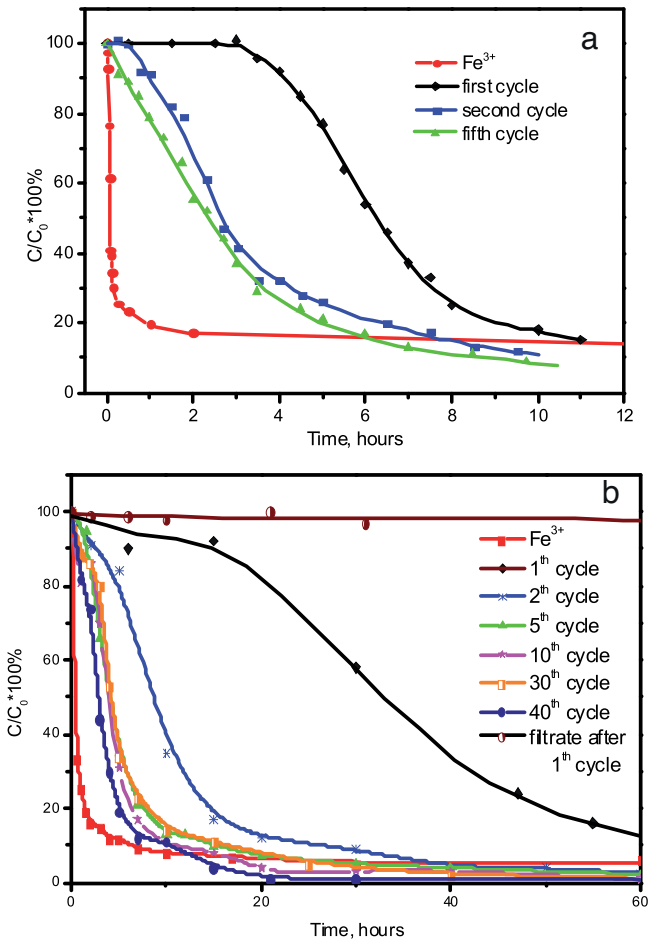

Fig. 5. Kinetic curves of phenol CWPO in the presence of dissolved iron nitrate ($[Fe^{3+}] = 10^{-4}$ M) and $LaFeO_3$ during long-term tests at 30 °C (a) and 50 °C (b) (pH 3).

not less active than the Cu-containing. It is reasonable to conclude that the $LaFeO_3$ undergoes activation through its interaction with the reaction medium. The reasons may be the following: (1) the products of the catalyst synthesis which block the active component are leached during the first and second cycles, and (2) the formation of new active sites on the catalyst surface after contact with the aqueous medium. To verify these hypotheses, we used physicochemical characterization of the catalysts before and after the reaction (see below). Table 2 gives the results of The analysis the solutions for contents of phenol and total organic carbon (TOC) after the first, second and fifth cycles showed the phenol conversions equal to 85, 88 and 91%, respectively, that also may be considered the evidence of the catalyst activation during the first and second cycles. However, the TOC conversion of 21–22 % was unchanged. The phenol concentration decreased to zero but the TOC conversion increased to 34–36% after the 25 h reaction. Further the reaction took 96 h (cycle 5) allowed the TOC conversion to be increased up to 52%.

Table 2
Conversion of phenol and total organic carbon (TOC) in the CWPO of phenol over $LaFeO_3$ (pH 3, 30 °C).

No. of cycle	Reaction time, hours	X_{PhOH}, %	X_{TOC}, %
1	10	85	21
	25	100	36
2	10	88	21
	25	100	34
5	10	91	22
	25	100	35
	96	100	52

The $LaFeO_3$ was undergone to 40 cycle testing at 50 °C in order to accelerate the reaction and to study the stability of the catalytic properties and the catalyst structure at high temperature (Fig. 5b). The induction period (ca. 20 min) was observed (both at 30 and at 50 °C) over the fresh catalyst and then shortened to 3–7 min during the second and the subsequent cycles. The specific catalytic activity was 2.3 mmol h^{-1} g_{cat}^{-1} in the first, 7.3 mmol h^{-1} g_{cat}^{-1} in the second cycle and varied between 12.9 and 16.6 mmol h^{-1} g_{cat}^{-1} in the subsequent cycles. The TOC conversion was 30.2 and 37.1% in the first and second cycles, respectively, and increased to 37.7–44.7% in the subsequent cycles. The quantities of iron and lanthanum leached from the catalyst varied as follows: 0.057–0.260 mM Fe (0.27–1.25% of the total iron in the catalyst); 0.091–0.158 mM La (0.45–0.78% of the total lanthanum in the catalyst). Any regular variations in the leached metal quantities were not observed from cycle to cycle, it seems like these were a total of errors of ±0.1 mM in measuring the concentrations.

Notice that the catalyst was dried and subjected to thermal treatment after 10th, 20th and 30th cycles of oxidative destruction of phenol but used wet without additional treatment in the rest cycles. This is an evidence that the catalyst under study does not need regeneration for at least ten successive cycles, i.e., intermediate products of phenol oxidation do not deposit in noticeable quantities to cause the surface coking and deactivation.

It is well-known the deposition of organics of the catalyst surface and blocking the active catalyst sites is possible indeed due to the side reaction of phenol oxidative polycondensation. As a result of the polycondensation the catalyst changes color from beige to black that indicates a high degree of the sample carbonization. In this work the catalyst preserves its original beige color and activity even after forty reaction cycles that leads to conclude about the absence of the carbonization. To confirm this conclusion we analyzed $LaFeO_3$ catalyst after forty reaction cycles by TPD method with MS detection of CO_2 and H_2O (Fig. S2). The analysis showed that the catalyst heated in air lost no more than ~9% of the total weight. This weight loss was due to the removal of water (thermal effect at 127 °C) and CO_2 (thermal effects at about 290, 400 and 730 °C). Similar effects were observed by thermal heating lanthanum oxide after exposure to air in works [39]. The data indicate the presence of water and carbonate within the surface layer of the catalyst after the reaction and the formation of lanthanum and iron oxides under the influence of the reaction medium. This consumption was confirmed by the XPS results (Section 3.6).

Thus, the perovskite-like $LaFeO_3$ catalyst does not lose the activity during forty oxidation cycles but is activated after the first and second cycles. The observed leaching of negligible metal quantities has not affected the catalyst activity. Apparently the low-active metal species are leached or the metals transfer to the solution as a result the catalyst attrition. The observed changes in the structure of the catalyst surface did not reduce the catalytic activity of the samples, but even increased it, possibly due to the formation of dispersed particles of iron oxide on the surface.

3.4. Leaching tests and homogeneous oxidation in the presence of Fe^{3+} ions

The key problem in the application of solid catalysts for liquid-phase processes (in particular in aqueous media) is the contribution of active metal ions leached from the solid catalyst to the total catalytic activity [40,41]. Leaching tests (Fig. 5b) and kinetic studies of phenol oxidation in the presence of iron nitrate solute (Fig. 5) were used for answering the question.

The leaching test was performed using the filtrate after tenth cycle of the reaction over $LaFeO_3$ at 50 °C (Fig. 5b). The decrease

Table 3
Phase composition and specific surface area of the perovskite-like samples $LaBO_3$ (B = Mn, Cu, Ni, Fe, Co).

Sample	Phase composition	S_{BET}, $m^2\,g^{-1}$
$LaCuO_3$	$LaCuO_3$ (orthorhombic)	5.6
$LaFeO_3$	$LaFeO_3$ (orthorhombic)	5.6
$LaCoO_3$	$LaCoO_3$ (hexagonal)Co_3O_4 (impurity amount)	1.8
$LaNiO_3$	$LaNiO_3$ (hexagonal)	4.7
$LaMnO_3$	$LaMnO_3$ (hexagonal)	3.2

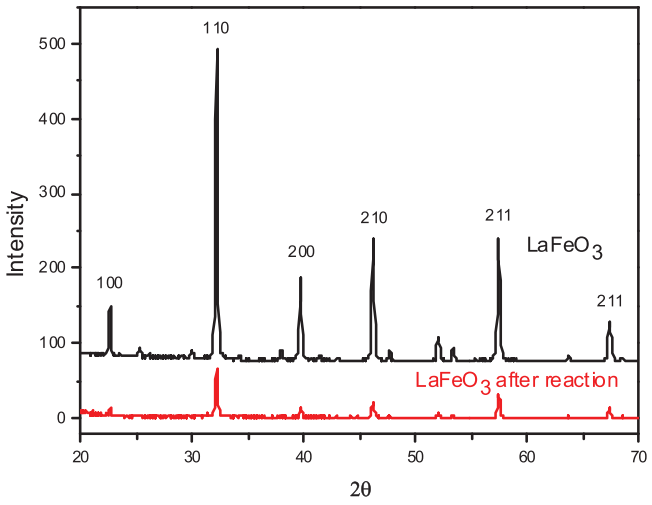

Fig. 6. Diffraction patterns of fresh and spent $LaFeO_3$ catalysts.

of the substrate concentration was not observed. Hence, iron compounds comprised in the perovskite-like oxide but not iron ions leached to the solution are responsible for the activity of $LaFeO_3$.

The phenol oxidation at 30 and 50 °C in the presence of dissolved iron nitrate (0.1 mM that is almost equal to the concentration of iron ions leached from the catalyst) showed that the reaction rate was, initially, higher in the homogeneous system there the maximal conversion was 85% at 30 °C and 92% at 50 °C (Fig. 5). In the heterogeneous system, phenol was oxidized completely. Apparently the formation complexes between iron ions and intermediates of phenol oxidation leads to deactivation the dissolved catalyst [34].

3.5. Catalyst studies using XRD and low temperature nitrogen adsorption

Generally, important parameters of solid catalysts are their specific surface area and extended porous structure. This often is not the case of liquid-phase catalytic processes when either geometric surface of the catalyst or the thin surface layer of granules are involved in the reaction due to diffusion and spatial limitations. The specific surface area of perovskite-like oxides under study varied from 1.8 to 5.6 $m^2\,g^{-1}$ (Table 3), rather extended porous structure being characteristic of the particles. Thus, the texture of the perovskite-like oxides is thought appropriate for liquid-phase processes.

From XRD data (Table 3, Fig. S3), oxides $LaBO_3$ (B = Cu, Fe, Mn, Ni, Co) are monophase perovskites with the orthorhombic or hexagonal crystal lattice. In $LaCoO_3$, there were detected Co_3O_4 impurities along with the main perovskite phase.

XRD studies of the catalyst after the reaction did not reveal changes in their phase composition. Irrespectively of their catalytic behavior all the samples preserved their perovskite structures. Less intense but not broadened reflections were only observed in the diffraction patterns of the $LaFeO_3$ sample used for 40-cycle testing (Fig. 6). This may be accounted for the small quantity of the sample available after the tests and used for XRD studies.

Thus, all the studied perovskite-like oxides are quite stable in aqueous media; activation of the Fe-containing catalyst cannot result from changes in its phase composition in the course of the reaction. The destroy of perovskite-like structure also may not be the reason for Mn-, Ni-, Co-containing perovskites to be catalytically inactive.

3.6. XPS studies of the catalysts

XRD studies did not reveal changes in the phase composition of the catalysts after the reaction. Hence XPS technique was used for studying the perovskite surface, in particular the electron state of elements. The XPS data acquired with $LaFeO_3$ and $LaCuO_3$ after the first oxidation cycle were compared to the results on the fresh catalysts.

Atomic concentration ratios of elements on the catalyst surface were calculated from the XPS spectra (Table 4). The oxygen content was found to increase after the reaction on the surface of both catalysts. The iron and lanthanum to oxygen ratios were 1.5 and 1.2 times decreased, respectively, on the surface of $LaFeO_3$, copper and lanthanum to oxygen ratios 2.7 and 1.17 times decreased, respectively, on the surface of $LaCuO_3$. In addition, Fe/La and Cu/La ratios on the catalyst surface decreased after the reaction by the values of 1.3 and 2.3 for Fe and Cu, respectively. These results are not in full agreement with the data of chemical analysis of the solutions after the reaction; the latter demonstrated that the metal stability in perovskites decreases in the series: Fe > La > Cu. However, it should be kept in mind that XPS data relate only to the catalyst surface. There were observed less changes in Fe/La and La/O ratios ($LaFeO_3$) than in Cu/La and La/O ratios ($LaCuO_3$); hence, the former catalyst is more stable than the latter.

Comparison of photoelectron spectra of levels Fe2p, Cu2p, La3d and O1s (Figs. 7–9) acquired with the fresh and spent catalysts leads us to conclude about changes in the electron states of metals and oxygen on the catalyst surface. Analysis of Cu2p spectrum of fresh $LaCuO_3$ (Fig. 8) revealed a binding energy of Cu2p level (933.6 eV) characteristic for the Cu^{2+} state [42,43]; hence, copper is preferably in the Cu^{2+} state in the fresh catalyst. The Cu2p peak (E_b = 932.6 eV) in the spectrum of the spent $LaCuO_3$ sample may be assigned both to copper metal and Cu^{1+}. The correct identification of the chemical copper state requires application of the so-called Auger parameter which is the sum of E_b(Cu2p) and E_{kin}(Cu LMM). The Auger param-

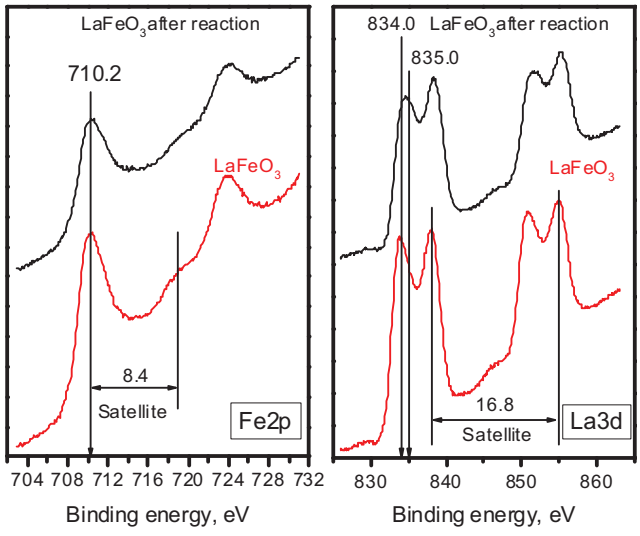

Fig. 7. Fe2p and La3d spectra of fresh $LaFeO_3$ and $LaFeO_3$ after CWPO of phenol.

Table 4
Ratio of atomic concentrations of elements calculated from XPS data on the fresh and spent $LaFeO_3$ and $LaCuO_3$ catalysts.

Sample		Fe/La	Cu/La	Fe/O	La/O	Cu/O
$LaFeO_3$	Fresh	0.50	–	0.06	0.13	–
	After the reaction	0.39	–	0.04	0.11	–
$LaCuO_3$	Fresh	–	0.53	–	0.14	0.08
	After the reaction	–	0.24	–	0.12	0.03

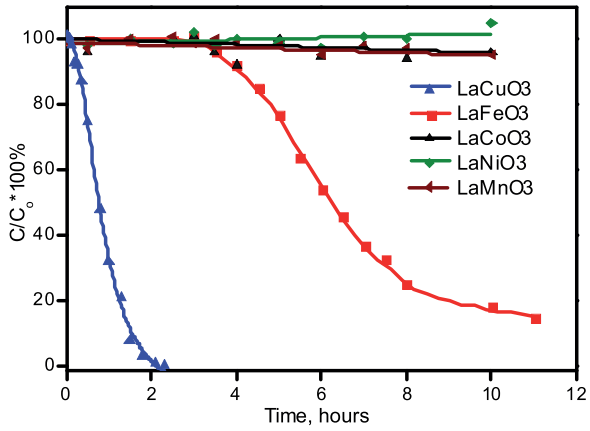

Fig. 8. Cu2p and La3d spectra of fresh $LaCuO_3$ and $LaCuO_3$ after CWPO of phenol.

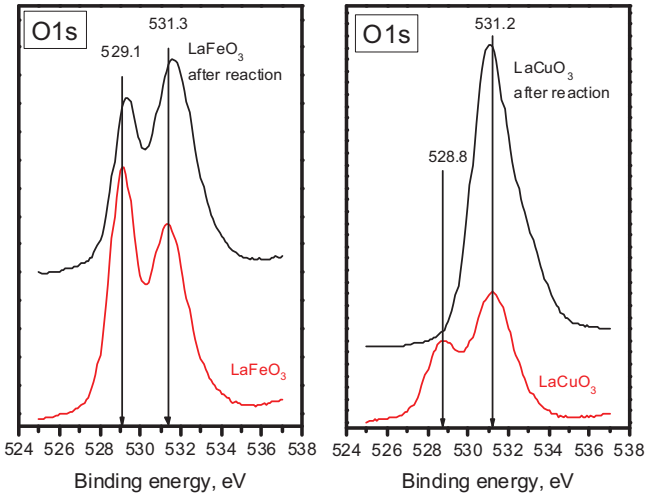

Fig. 9. O1s spectra of fresh $LaFeO_3$ and $LaCuO_3$ and catalysts after CWPO of phenol.

eter is sensible to the chemical state of copper and independent of relaxation processes in the course of electron photoemission and sample charging [31]. After the reaction, the Auger parameter of $LaCuO_3$ is characterized by the value of 1847.9 eV that is characteristic of the copper state Cu^{1+}. Since this parameter of copper metal is 1851.4 eV, it is reasonable to assume that there are two copper states, Cu^{1+} and Cu^{2+}, on the catalyst surface after the reaction. The Cu^{1+} is responsible for the generation of peroxide radicals as strong oxidants following the mechanism similar to that in the Raff system (Fe^{3+}/ H_2O_2, Scheme 1) [34].

Cu^{2+} state is characteristic of copper in perovskite unlike iron and regardless of stoichiometry ($LaBO_3$). Hence, there is some special electron state of this oxide system, which allows overlapping of the copper and oxygen levels to decrease the charge on both copper and oxygen and, therefore, to favor the process of copper reduction. While the oxide phase composition does not change, Cu^{1+} is only formed on the surface. Again, the presence of oxygen

$$Fe^{3+} + H_2O_2 \rightleftharpoons FeHO_2^{2+} + H^+$$
$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$$
$$FeHO_2^{2+} \longrightarrow Fe^{2+} + HO_2^{\bullet}$$
$$FeHO_2^{2+} + FeOH^{2+} \longrightarrow 2Fe^{2+} + O_2 + H_2O$$
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

Scheme 1. Mechanism of the reactions in the Raff system (Fe^{3+} /H_2O_2).

bridges between neighboring copper ions is thought to facilitate the transfer from Cu^{2+} to Cu^{1+} and to stabilize this state.

Analysis of the Fe2p spectra of fresh and spent $LaFeO_3$ samples (Fig. 7) revealed the line with the binding energy (E_b = 710.2 eV) and shape characteristic of the Fe^{3+} state [31,43,44]. In the spectrum of Fe^{2+}, there is a strongly pronounced shake-up satellite at a distance of 6 eV higher than the main Fe2p line are observed in the Fe^{3+} spectra, but these satellites are much less intense and shifted farther (ca. 8–9 eV) from the main peak of iron. Supposedly, the above described mechanism similar to that in the Raff system (Scheme 1) also is characteristic of the system under consideration and implies the transfer from Fe^{3+} to Fe^{2+}. The absence of lines of Fe^{2+} in the spectra of spent catalysts may be accounted for by its fast oxidation in air to the initial Fe^{3+} state that is characteristics of iron ions in the perovskite structure.

Analysis of the photoelectron spectrum La3d (Figs. 4 and) reveals the presence of intense lines of the shake-up satellite (E_b = 838.0 and 856 eV) and the spin-orbit splitting between peaks $La3d_{5/2}$ and $La3d_{3/2}$ equal to 16.8 eV that leads us to conclude about predominant state La^{3+} in the complex oxide. However, the binding energy of 834.0 eV relates to lanthanum in the perovskite structure and binding energies of ~835 eV are characteristic of the oxide (La_2O_3) and hydroxide ($La(OH)_3$). In addition, there may be lanthanum carbonate on the surface [43,45]. We can assume that the perovskite lanthanum predominates in the fresh $LaFeO_3$ but the surface superposition of the said states is observed in the fresh $LaCuO_3$ and in the spent catalysts $LaFeO_3$, $LaCuO_3$.

Two components (E_b = 529, 530.8–531.5 eV) and a weakly intense peak at E_b≈533 eV are identified in the O1s spectra of the samples under study (Fig. 9). Literature analysis showed that the oxygen states in perovskite-like systems are rather complex and ambiguous to interpret. Nevertheless, the O1s peak at the lowest binding energy may be assigned to the lattice oxygen O^{2-} and the peak at E_b = 530.8–531.5 eV is characteristics of hydroxyl and carbonate species on the catalyst surface, while the peak at the highest binding energy is assigned to water molecules adsorbed on the surface [43–47].

Detection of hydroxyl groups and water molecules on the surface of spent catalysts is not surprising, they may account for an increase in the oxygen content on the catalyst surface after the reaction. This is the formation of these species that may be the reason for higher catalytic activity of the perovskites after the first and second catalytic cycles because water and hydroxyl groups are involved directly in the mechanism of peroxide oxidation (Scheme 1). The carbonate species may form due to the adsorption of the organic

substrate and of its intermediate oxidation products followed by their complete oxidation.

4. Conclusions

Perovskite-like transition metal oxides $LaBO_3$ (B = Mn, Fe, Cu, Ni, Co) were synthesized by the Peccini method and tested as catalysts for CWPO of phenol. The catalytic activity to the reaction was only observed with Fe- and Cu-containing perovskites, $LaCuO_3$ being more active than $LaFeO_3$. At the same time, $LaFeO_3$, in addition to its high catalytic activity, was rather stable to leaching of the active component during forty cycles of catalytic tests. An induction period was observed in the first cycle of the reaction catalyzed by $LaFeO_3$ but shortened considerably in the second and succeeding cycles. XRD studies of the spent catalysts demonstrated the stability of the perovskite-like structures of all the samples in the aqueous oxidative medium. Comparative XPS studies of $LaCuO_3$ and $LaFeO_3$ before and after the reaction allowed us to conclude about redox transitions Cu^{2+}/Cu^{1+} and Fe^{3+}/Fe^{2+}, respectively, of the catalytically active metals. An increase in the surface concentrations of oxygen-containing species (hydroxyl groups and water), which were involved in the transformations, was the reason for a noticeable shortening of the induction period during the second and succeeding cycles. Hence, $LaCuO_3$ and $LaFeO_3$ are promising catalysts for complete oxidation of organic substrates with hydrogen peroxide in aqueous solutions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015.05.055

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